A comparison of high-Au massive sulfide ores hosted in ophiolite complexes of the Balkan Peninsula with modern analogues: Genetic significance

Maria Economou-Eliopoulos a,⁎, Demetrios G. Eliopoulos b, Stephan Chryssoulis c

a Department of Geology, University of Athens, Panepistimiopolis, 15784 Athens, Greece
b Institute of Geology and Mineral Exploration, 70 Messoghion Street, GR-11527 Athens, Greece
c AMTEL, 100 Collip Circle, UWO Research Park, London, ON, Canada N6G 4X8

Received 25 July 2005; accepted 21 October 2006
Available online 9 February 2007

Abstract

Ophiolites of the Balkan Peninsula, of Upper Jurassic to Lower Cretaceous age, extend through the Mirdita zone (Albania) to the Pindos and Othrys complexes southern (Greece), and host massive sulfide deposits of Cu–Zn–(Pb) type. The deposits in Albania are hosted in intermediate to felsic-dominated volcanic successions of considerable thickness. These deposits are associated with ophiolites that were formed during the initial stages of an intra-oceanic westward-dipping subduction zone (arc, fore-arc, back-arc setting), and most closely resemble polymetallic sulfide deposits associated with felsic volcanic rocks at the modern seafloor. The massive sulfide ores are comprised of pyrite, chalcopyrite and lesser amounts of sphalerite, and are characterized by an increasing content of Au, Ag, As, Se, Sb, Mo and Hg from the Othrys to Pindos and Mirdita (Munella) ophiolites. In addition, the concentrations of these elements in both massive sulfide ores and Fe–Cu–Ni–Co type ores are higher in the Pindos compared to those in the Othrys complex.

Sulfide mineralization associated with these complexes differs from the majority of Cyprus-type deposits in terms of: (a) host rock-type; (b) mineralogical composition, i.e., the presence of tennantite–tetrahedrite series minerals in the Mirdita sulfide ores, and the selenide clausethalite, hosted exclusively within later stage chalcopyrite and sphalerite intergrowths in the Pindos ores; and (c) their enrichment in Au. Gold in both Pindos and Mirdita ores occurs as submicroscopic gold, including solid solution gold, colloidal gold and surface-bound gold, in arsenian pyrite, chalcopyrite and bornite grains, and rarely as fine-grained electrum. The increasing Au content (up to 15.1 ppm) with decreasing crystal size in fine intergrowths between pyrite and sphalerite may be related to remobilization and re-deposition. However, submicroscopic gold in coarse-grained pyrite of the main mineralization stage (mean concentrations up to 1.01 ppm in the Pindos ores and 0.22 ppm in the Mirdita ones) may be co-precipitated into the structure of arsenian pyrite, reflecting the direct involvement of magmatic volatiles to the ore-forming hydrothermal system rather than recrystallization effects, and in turn the precious metal endowment in the hydrothermal systems.

The Mirdita and Pindos massive sulfide ores are comparable to some modern seafloor deposits in terms of their association with andesitic pillow lavas and intermediate to felsic volcanic rocks and their bulk composition and mineralogy.

© 2007 Elsevier B.V. All rights reserved.

Keywords: Ophiolite; Submicroscopic gold; Pindos; Mirdita; Balkan Peninsula; Greece; Albania
1. Introduction

During the last three decades, after discovery of hydrothermal vents at mid-oceanic ridges, a significant number of volcanic-associated massive sulfides (VMS) have been described in a variety of tectonic settings on the modern seafloor. Excellent descriptions of modern seafloor sulfides and related vent fluids have provided valuable information for the improved understanding of ancient sulfide deposits associated with ophiolite complexes (e.g., Franklin et al., 1981; Hannington et al., 1998; Galley and Koski, 1999; Herzig et al., 2003; Franklin et al., 2005).

High gold contents, which were previously well known only in epithermal deposits on the continents, were found in ancient VMS and modern seafloor sulfide deposits. It has been subsequently confirmed that seafloor hydrothermal systems are capable of transporting and depositing significant amounts of gold (Herzig et al., 1993; Herzig and Hannington, 1995; Hynes, 1972). The presence of both lherzolite and harzburgites, lherzolites, gabbros and pillow lavas has been derived from different mantle sources and/or various degrees of partial melting (Pearce et al., 1984; Jones and Robertson, 1991; Ohnenstetter et al., 1999; Shallo, 1994; Saccani and Photiadis, 2004).

The Pindos complex tectonically overthrusts Eocene flysch of the Pindos zone. The complex contains a spectrum of lavas from MOR basalts through island arc tholeites (IAT) to boninite series volcanics (BSV). Two tectonically distinct ophiolitic units can be distinguished: (a) the upper unit (Dramala Complex), including mantle harzburgites and (b) a lower unit, including an intrusive (alternation of troctolites with various ultramafic rock-types) and the volcanic and subvolcanic sequence, which is represented by the Aspropotamos Complex (Fig. 1). Both units share similar metamorphic soles and tectono-sedimentary mélanges at their base. Ophiolitic slices (mafic rocks) sandwiched between the Aspropotamos unit and underlying Avdella mélange display contrasting geochemical signatures. The different magmatic groups may have been derived from different mantle sources and/or various degrees of partial melting (Pearce et al., 1984; Kostopoulos, 1989; Jones and Robertson, 1991).

The ophiolites of the Balkan Peninsula are an important component of the Upper Jurassic to Lower Cretaceous Tethyan ophiolite belt, which extends through the Mirdita zone to the Pindos and Othrys complexes in the south (Subpelagonian zone) and to the Serbian zone of the Dinarides in the north. The ophiolites have a NNW–SSE strike, and outcrop in a discontinuous and narrow belt to the west of the Pelagonian Massif (Economou-Eliopoulos, 1996).

2. Geotectonic setting of ophiolites

The ophiolite complexes of the Balkan Peninsula; their genetic significance is discussed.
more than one stage. Features indicative of both MOR- and supra-subduction zone (SSZ) type have been attributed to a back-arc basin environment (Hynes, 1972; Rassios, 1990; Economou-Eliopoulos, 1996).

The Albanian ophiolites can be divided into two NNW–SSE trending sub-parallel belts, the western ophiolite belt (WOB) and eastern ophiolite belt (EOB), both of which have mid-ocean ridge and island arc
affinities, respectively (Fig. 2). The Mirdita ophiolite belongs to the eastern ophiolite belt, which is 6 to 8 km thick and has been dismembered into several large massifs. The magmatic sequences of these ophiolites show a wide lithological variation, including low-Ti and very low-Ti magmatic sequences. They are mainly composed by ultramafic cumulates, layered gabbros, massive gabbros, diorites and plagiogranites. The chemical composition of the sheeted dikes is close to that of the volcanic analogues of the basalt–dacitic series showing a transitional tholeiitic to calc-alkaline affinity. The Mirdita ophiolites are similar to the Pindos complex, which can be considered as a prolongation of the former. They share many petrological and geochemical characteristics and have been explained as forming by oceanic spreading above an intra-oceanic subduction zone during the Late Jurassic, with further uplift during the Tithonian to Lower Cretaceous (Shallo, 1994; Robertson and Shallo, 2000; Saccani and Photiadis, 2004; Hoxha et al., 2005).

3. Local geology

3.1. Aspropotamos area, Pindos ophiolite complex

Sulfide mineralization in the Pindos ophiolite complex is located in the Smolicas Mountains, near the Aspropotamos dismembered ophiolite unit. This sequence belonging to the lower ophiolitic unit of the Pindos complex and includes: (a) an intrusive section composed of dunites, lherzolites, olivine-websterites, olivine-gabbros, anorthosite gabbros, gabbros and

Fig. 2. (A) Sketch map showing the location of major sulfide deposits in the Mirdita ophiolite Massif, Albania. (B) Simplified geological map of the Munella sulfide deposit (after Hoxha et al., 2005).
occasionally gabbronorites; and (b) a volcanic and subvolcanic sequence composed mainly by basalts and basaltic andesite pillow lavas ranging from high- to low-Ti affinity (Pearce et al., 1984; Kostopoulos, 1989; Jones and Robertson, 1991; Saccani and Photiadis, 2004).

The Aspropotamos pillow lavas are aphyric to plagioclase-porphyrritic with laths of plagioclase and interstitial clinopyroxene. Massive lavas are mostly basaltic andesites with clinopyroxene and minor plagioclase phenocrysts in an intergranular groundmass containing microlites of clinopyroxene and plagioclase. 

Due to tectonic disruption of the Aspropotamos unit, the spatial association between massive and stockwork-disseminated mineralization is unclear. Nevertheless, numerous of sub-vertical veins of quartz with veinlets and disseminations of pyrite + chalcopyrite, a few m in thickness, cut diabase. Also, a brecciated pipe-shaped diabase dike (200 m×50 m), with a vertical extent of 150 m, is found in the Neropriona area of the Aspropotamos unit, Kondro Hill, very close to the village of Perivoli (Fig. 2). This hydrothermal breccia is present in both pillow and massive lavas. Albite, prehnite and minor calcite and actinolite are common alteration products (Saccani and Photiadis, 2004).

3.3. Mirdita complex

The volcanic rocks of the Mirdita ophiolites have been sub-divided into two successions: (a) the Middle to Late Jurassic lower basalt–andesite succession, consisting mainly of pillow lava and occasionally massive flows, 1 to 1.5 km in thickness, injected by a dolerite, and a dacite–rhyolite (keratophyre) sheeted dyke complex; and (b) the Late Jurassic upper succession consisting of andesite, basalt and dacite (boninite) volcanoclastic succession, about 700 m thick, containing occasional pillow lavas. This sequence is overlain by spherulitic, microlitic dacite and rhyodacite–rhyolites, pyroclastics and volcanic glasses. Finally, the whole sequence is overlain by Mn-bearing radiolarian chert, 1 to 10 m thick (Shallo, 1994; Hoxha et al., 2005).

4. Methods of investigation

Trace elements were determined at X-ray Assay Laboratories (XRAL), Ontario, Canada, using ICP/MS methods. Selenium was analyzed using the atomic absorption/hydride system, with a detection limit of 0.1 ppm. Platinum, Pd and Au were analyzed after preconcentration by the Lead Fire Assay technique from large (30 g) samples. Detection limits are 1 ppb for Pd and Au, 10 ppb for Pt.

Polished thin sections were investigated by optical microscopy and scanning electron microscopy. Electron microprobe analyses were carried out at the University of Athens, using a JEOL JSM-5600 SEM equipped with an Oxford ISIS 300 Energy Dispersive System, with the following operating conditions: accelerating voltage 20 kV, beam current 0.5 nA, count time 50 s and a beam diameter of 1 to 2 μm.

Microbeam techniques used to characterize and quantify submicroscopic gold in polished sections include Secondary Ion Mass Spectroscopy (SIMS) and Time of Flight-Resonant Ionization Mass Spectroscopy (TOF-RIMS). Analysis of 96 sulfide grains was carried out at Advanced Mineral Technology Laboratory (AMTEL), London, Ontario, using a Cameca IMS-3f ion probe and following the analytical and standardization procedures.
Table 1
Geochemical characteristics of sulfide ores hosted in ophiolite complexes and those from the modern seafloor

<table>
<thead>
<tr>
<th>Main minerals</th>
<th>ppm</th>
<th>ppb</th>
<th>wt.%</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pt</td>
<td>Pd</td>
<td>Ag</td>
<td>Au</td>
</tr>
<tr>
<td>Pindos</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Kondro: massive ore consisting of pyrite (py), chalcopyrite (cpy), sphalerite (sph), bornite (bn)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>py–cpy</td>
<td>&lt;10</td>
<td>4</td>
<td>56</td>
<td>1.1</td>
</tr>
<tr>
<td>py–cpy</td>
<td>&lt;10</td>
<td>3</td>
<td>34</td>
<td>1.3</td>
</tr>
<tr>
<td>py–cpy–sph</td>
<td>&lt;10</td>
<td>3</td>
<td>38</td>
<td>3.3</td>
</tr>
<tr>
<td>py–cpy–sph</td>
<td>&lt;10</td>
<td>4</td>
<td>32</td>
<td>3.6</td>
</tr>
<tr>
<td>py–bn–cpy</td>
<td>&lt;10</td>
<td>3</td>
<td>39</td>
<td>3.2</td>
</tr>
<tr>
<td>Aspropotamos (Neropriona): disseminated pyrite (py), chalcopyrite (cpy)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Diabase breccia</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>less altered</td>
<td>&lt;10</td>
<td>10</td>
<td>0.011</td>
<td>&lt;5</td>
</tr>
<tr>
<td>moderately altered</td>
<td>400</td>
<td>20</td>
<td>0.018</td>
<td>&lt;5</td>
</tr>
<tr>
<td>highly altered</td>
<td>1000</td>
<td>27</td>
<td>0.025</td>
<td>&lt;5</td>
</tr>
<tr>
<td>Quartz veins (Aspropotamos): disseminated pyrite (py), chalcopyrite (cpy), pyrrhotite (po)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>&lt;10</td>
<td>10</td>
<td>0.15</td>
<td>130</td>
<td>20</td>
</tr>
<tr>
<td>0.018</td>
<td>&lt;5</td>
<td>25</td>
<td>&lt;5</td>
<td>0.3</td>
</tr>
<tr>
<td>0.025</td>
<td>&lt;5</td>
<td>25</td>
<td>&lt;5</td>
<td>0.6</td>
</tr>
<tr>
<td>Tsoumes: massive ore consisting of pyrrhotite (po), pyrite (py), pentlandite (pn), chalcopyrite (cpy), magnetite (mt)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>po–py–pn–cpy–mt</td>
<td>&lt;10</td>
<td>15</td>
<td>0.15</td>
<td>130</td>
</tr>
<tr>
<td>po–py–pn–cpy–mt</td>
<td>20</td>
<td>3</td>
<td>0.14</td>
<td>350</td>
</tr>
<tr>
<td>po–py–pn–cpy–mt</td>
<td>&lt;10</td>
<td>10</td>
<td>0.11</td>
<td>95</td>
</tr>
<tr>
<td>Othrys</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cyprus-type</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mathiati</td>
<td>45</td>
<td>4</td>
<td>0.8</td>
<td>20</td>
</tr>
<tr>
<td>Albania</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mirdita-Munella</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>py–cpy</td>
<td>2</td>
<td>4</td>
<td>1.4</td>
<td>90</td>
</tr>
<tr>
<td>cpy</td>
<td>2</td>
<td>4</td>
<td>0.9</td>
<td>980</td>
</tr>
<tr>
<td>sph–cpy</td>
<td>2</td>
<td>120</td>
<td>66</td>
<td>3</td>
</tr>
<tr>
<td>NE Pacific Ridge</td>
<td>28</td>
<td>105</td>
<td>0.8</td>
<td>114</td>
</tr>
<tr>
<td>TAG mid-Atlantic Ridge</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pyrite–chalcopyrite</td>
<td>17</td>
<td>17</td>
<td>0.56</td>
<td>177</td>
</tr>
<tr>
<td>massive pyrite</td>
<td>10</td>
<td>37</td>
<td>1.43</td>
<td>11</td>
</tr>
<tr>
<td>Pyrite–sphalerite</td>
<td>23</td>
<td>450</td>
<td>5.6</td>
<td>1</td>
</tr>
<tr>
<td>Indian ocean floor</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>chalcopyrite</td>
<td>3</td>
<td>30</td>
<td>0.06</td>
<td>450</td>
</tr>
<tr>
<td>pyrite–marcasite</td>
<td>3</td>
<td>30</td>
<td>0.13</td>
<td>125</td>
</tr>
<tr>
<td>sphalerite</td>
<td>3</td>
<td>4</td>
<td>0.08</td>
<td>9</td>
</tr>
</tbody>
</table>

References: (1) this work; (2) Economou-Eliopoulos and Eliopoulos (1998); (3) Hannington et al. (1998); (4) Halbach et al. (1998).
given by Chryssoulis et al. (1989). Operating parameters for SIM analysis were: Cs⁺ as primary beam, ¹⁹⁷Au⁻, ⁵⁶Fe⁻ secondary ions monitored, and elimination of molecular interferences by voltage offset (180 V). The detection limit was 0.20 ppm Au. In TOF-RIMS, after laser ablation, only one specific atomic species is resonantly (i.e., selectively) excited and ionised by a second tunable laser source. Analytical spot size was 30 μm in diameter, sampling depth was 0.01 μm, and detection limit of 0.01 ppm Au.

5. Mineralogical and geochemical characteristics of the sulfide ores

5.1. Pindos

5.1.1. Massive sulfide ores of Cyprus-type

Massive sulfide occurrences in the form of small lenses (maximum 4 by 40 m) are found at Kondro Hill on the SE slopes of Smolikas Mountain (Fig. 1). The estimated ore potential is ca. 10,000 tonnes with average 6.6 wt.% Cu and 9.4 wt.% Zn, (Skounakis et al., 1980). They occur on top of diabase (massive or pillow lavas) and are directly overlain by Fe-oxide-bearing sediments. Fragments of limestone, entirely enclosed within massive ore, are occasionally present.

A salient feature of the Pindos massive ore from Kondro is the significant contents of Au (up to 3.6 ppm), Ag (up to 56 ppm), as well as high contents of Se (up to 1900 ppm), Co (up to 2200 ppm), Mo (up to 310 ppm), Hg (up to 280 ppm) and As up to 150 ppm (Table 1). The ore is mainly comprised of pyrite and chalcopyrite; bornite sphalerite, marcasite, covellite and siegenite are found in lesser amounts. Textural relationships indicate that early pyrite, commonly occurring as fractured, large crystals, is extensively replaced by chalcopyrite, and then by bornite in a matrix of quartz (Fig. 3). Pyrite is extensively replaced by intergrowths between chalcopyrite and Fe-poor (~ 1 wt.% Fe) sphalerite with an average Cu content of 0.5 wt.% or FTMS, then by bornite in a matrix of quartz (Fig. 3). Copper-bearing sphalerite, with up to 3.6 wt.% Fe and 3.2 wt.% Cu, cements minor chalcopyrite and pyrite (Table 2). Pyrite is extensively replaced by intergrowths between chalcopyrite and Fe-poor (~ 1 wt.% Fe) sphalerite with an average Cu content of 0.5 wt.% or FTMS, then by bornite in a matrix of quartz (Fig. 3). Copper-bearing sphalerite, with up to 3.6 wt.% Fe and 3.2 wt.% Cu, cements minor chalcopyrite and pyrite (Table 2). Pyrite is extensively replaced by intergrowths between chalcopyrite and Fe-poor (~ 1 wt.% Fe) sphalerite with an average Cu content of 0.5 wt.% or FTMS, then by bornite in a matrix of quartz (Fig. 3). Copper-bearing sphalerite, with up to 3.6 wt.% Fe and 3.2 wt.% Cu, cements minor chalcopyrite and pyrite (Table 2). Pyrite is extensively replaced by intergrowths between chalcopyrite and Fe-poor (~ 1 wt.% Fe) sphalerite with an average Cu content of 0.5 wt.% or FTMS, then by bornite in a matrix of quartz (Fig. 3). Copper-bearing sphalerite, with up to 3.6 wt.% Fe and 3.2 wt.% Cu, cements minor chalcopyrite and pyrite (Table 2).

Our investigation, using SIMS, reveals the presence of submicroscopic gold, i.e., < 1 μm and thus invisible under the optical microscope (including solid solution gold, colloidal gold and surface-bound gold), in grains of pyrite, chalcopyrite and bornite (Figs. 4 and 5; Tables 3 and 4). More specifically, the Au concentration in pyrite increases with (i) decreasing crystal size, and (ii) position in the paragenetic sequence (later grains are higher in Au), without any covariance whatsoever with the As content of pyrite. Concentrations of ‘invisible Au’ in coarse-grained pyrite (associated with chalcopyrite and bornite) range from 0.7±0.13 to 1.01±0.27 ppm, whereas concentrations in fine-grained pyrite lie between 7.67±1.6 and 5.3±2.7 ppm. In very fine intergrowths between pyrite and sphalerite, concentrations of 8.83±1.53 ppm were determined; fine intergrowths between pyrite and bornite gave 17.3±5.5 ppm (Table 3). These significant Au concentrations (>1 ppm), accompanied by significant As content, confirm the tendency for gold to be incorporated in As-bearing pyrite (Cook and Chryssoulis, 1990). Crystal facets and fracture surfaces of the coarse-grained pyrite from Pindos were analyzed using TOF-RIMS, a surface sensitive micro-analytical technique to document if there is more gold on the crystal facets. This was indeed found to be the case (6 versus 0.5 ppm; Figs. 4 and 5). The extremely small amounts of visible native gold observed in the Pindos sulfide ores, coupled with the relatively high concentration of invisible gold determined in fine-grained pyrite and gold on the crystal facets (Tables 3 and 4; Figs 4 and 5) strongly suggest that the majority of the gold is essentially found as structurally-bound gold in pyrite.

5.1.2. Disseminated pyrite within diabase breccia

In the brecciated diabase underlying the Kondro massive ore, disseminated pyrite and minor chalcopyrite occur mostly in vesicles filled by quartz, kaolinite, chlorite and epidote (Fig. 6). Remnants of pyrrhotite within pyrite, surrounded by Fe-hydroxides or magnetite suggest an evolution toward more oxidized conditions of the circulating seawater. The Pd content in breccia samples (10 to 27 ppb) is low compared to that of Pt (160 to 1000 ppb). The significant enrichment in Pt in kaolinite-rich samples, and the limited range of δ³⁴S values for pyrite concentrates from the diabase breccia (+1.0 to +1.5‰), are characteristic features (Table 1; Sideris et al., 1984).

5.1.3. Disseminated pyrite and chalcopyrite within quartz veins

In the Aspropotamos area (Fig. 1), sub-vertical veins of quartz with veinlets and disseminations of pyrite+
chalcopyrite, a few metres in thickness, cut diabase. Average metal contents are 10 wt.% Fe; 1.2 wt.% Cu, 50 ppm Co, 80 ppm Zn, 1.5 ppm Ag (up to 12 ppm) and 22 ppm As (Table 1). Gold, Mo, Sb and Hg contents are all <10 ppm. These zones are interpreted as the discharge pathways of relatively high-temperature hydrothermal fluids (Rassios, 1990). They are now largely oxidized by the transformation of chalcopyrite to

Fig. 3. Photomicrographs illustrating aspects of ore textures in massive sulfide ores from Pindos. Disseminated euhedral coarse-grained pyrite (py), extensively fragmented, in a matrix of Cu-minerals, mostly bornite (bn) and quartz (black) (a–e), pyrite overgrown by microcrystalline and fine-grained pyrite (a–h), intergrowths between chalcopyrite (cpy) and pyrite (f), and between pyrite and bornite (c and j), between pyrite, chalcopyrite and bornite (f) and between sphalerite (sph)–pyrite and bornite (j).
goethite and pyrrhotite to pyrite. Very fine grains of barite and galena are occasionally present.

5.1.4. Fe–Cu–Ni–Co type
Small irregular to lens-like occurrences (4 by 1.5 m) of massive sulfide mineralization of Fe–Cu–Ni–Co type are exposed at Perivoli (Tsoumes) Hill (Fig. 1A). These are hosted within gabbro, close to its contact with serpentinized harzburgite. The sulfide ore is mainly composed of pyrrhotite and pyrite. Troilite, Co-bearing pentlandite, chalcopyrite, mackinawite, malachite and azurite are present in lesser amounts. Co-bearing pentlandite occurs as small (<100 μm) inclusions within pyrrhotite. Pure magnetite, often forming a network texture, is associated with sulfides, either as massive ore with inclusions of sulfides (chalcopyrite, pyrite and pyrrhotite), or as individual grains dispersed within sulfide ore (Skounakis et al., 1980).

5.2. Othrys

5.2.1. Massive sulfide ores of Cyprus-type
The largest occurrences are found in the areas of Aghioi Theodoroi and Limogardi (ca. 25,000 tonnes). At Limogardi, massive sulfide ore, up to 5 m thick, overlies stockwork and disseminated sulfides. This zone is overlain by hydrothermally altered lava, with several veins of ferruginous chert (jasper) and disseminated pyrite. Remnants of sponge-textured silica-pyrite rocks (poroliths) are also present, as are sphalerite, chalcopyrite, pyrrhotite, epidote and barite. The average Cu content of massive ore is <2 wt.%, the maximum is 5% (Rassios, 1990; Robertson and Varnavas, 1993). Widespread Mn-rich ribbon radiolarites overlying the Othrys lavas have been interpreted as biogenic sediments mixed with Mn-oxides derived from high-temperature axial vents and/or off-axis low temperature vents (Robertson and Varnavas, 1993).

5.2.2. Fe–Cu–Ni–Co type
Small sulfide bodies consisting of pyrrhotite, chalcopyrite, and minor Co-pentlandite, and associated with pure magnetite, occur at the peripheries of podiform chromite bodies hosted in serpentinized harzburgite of the Eretria (Mavro) area, Othrys ophiolite complex. The compositions of host rocks, chromite and sulfides are inconsistent with the sulfides having reached equilibrium with their host rocks at magmatic temperatures. Accordingly, it has been concluded that they are of hydrothermal rather than magmatic origin (Economou and Naldrett, 1984).

Both Cyprus- and Fe–Cu–Ni–Co type massive sulfide ores from the Othrys ophiolite complex are characterized by much lower Au, Ag, Se, As, Sb, Hg and Zn contents in comparison with those of the corresponding sulfide mineralizations of the Pindos complex (Table 1).

5.3. Mirdita

Major sulfide orebodies in the eastern ophiolite belt occur in the central-northern part of Albania. They are hosted in the volcanic sequence, consisting of andesitic–basaltic pillowed and massive lavas, dacite, rhyodacite and rhyolite extrusives and their glassy and pyroclastic analogues (Shallo, 1994). The whole region has been affected by intense tectonism, resulting in faulting, overthrusting and internal disruption of ophiolites and accompanying mineralization. Integrated geological–geophysical exploration led to the identification of large sulfide (massive, stockwork and disseminated) ore deposits. The best outcrops are exposed

<table>
<thead>
<tr>
<th>Main minerals</th>
<th>Pyrite</th>
<th>Chalcopyrite</th>
<th>Sphalerite</th>
<th>Bornite</th>
<th>Clausthalite</th>
<th>Sb–Fe-sulphide</th>
</tr>
</thead>
<tbody>
<tr>
<td>Description</td>
<td>Coarse</td>
<td>Coarse</td>
<td>Coarse</td>
<td>Coarse</td>
<td>Coarse</td>
<td>Coarse</td>
</tr>
<tr>
<td></td>
<td>Stage I</td>
<td>Stage I</td>
<td>Stage I</td>
<td>Stage I</td>
<td>Stage I</td>
<td>Stage I</td>
</tr>
<tr>
<td>wt.%</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe</td>
<td>46.6</td>
<td>31.6</td>
<td>30.1</td>
<td>30.5</td>
<td>3.6</td>
<td>1.8</td>
</tr>
<tr>
<td>Cu</td>
<td>n.d.</td>
<td>33.4</td>
<td>34.8</td>
<td>35.3</td>
<td>3.2</td>
<td>0.8</td>
</tr>
<tr>
<td>Zn</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>n.d.</td>
<td>59.9</td>
<td>64.2</td>
</tr>
<tr>
<td>S</td>
<td>53.1</td>
<td>34.2</td>
<td>34.1</td>
<td>33.1</td>
<td>33.5</td>
<td>32.3</td>
</tr>
<tr>
<td>Total</td>
<td>99.7</td>
<td>99.2</td>
<td>99</td>
<td>100</td>
<td>100.2</td>
<td>99.1</td>
</tr>
</tbody>
</table>

n.d. = below detection limit.

Table 2
Electron microprobe analyses of ore minerals from massive sulphide ores of the Pindos ophiolite complex

89
at Munella, Gurth Spach, Spach and Lak Rosh (Fig. 2A). Estimated reserves are 10,000 tonnes (at 1.0 wt.% Cu) for the Spach deposit, 8,800 tonnes (at 1 wt.% Cu and 0.7 wt.% Zn, 0.7 ppm Au and 15 ppm Ag) for the Munella deposit, and 2,700 tonnes (at 1.2 to 1.9 wt.% Cu) for the Gurth Spach and Lak Roshi deposits (Kyritsis, 1993; Deda et al., 1995; Shallo and Gjata 1995; Hoxha et al., 2005).

Fig. 4. TOF-RIMS spectrum of (a) fracture surface of coarse pyrite, (b) coarse pyrite crystal facet, and (c) fine/microcrystalline pyrite.
There is a significant continuation of orebodies occurring in multiple mineralization horizons in both the lower lava-dominated, and upper pyroclastic volcanic successions. Massive sulfide pyrite–chalcopyrite ores underlain by disseminated veins and stockworks are hosted by a Middle to Upper Jurassic lower basalt–andesite succession at Spach and Lak Rosch. The Lak Rosch orebody is mainly composed by chalcopyrite and pyrite, with lesser sphalerite, magnetite, galena, bornite and tennantite–tetrahedrite. The Upper Jurassic, upper dacite volcanoclastic, andesite–dacite, boninite succession hosts massive pyrite–chalcopyrite–sphalerite ore underlain by few or no disseminated veins or stockworks at Gurth Spach, Munella and Chafe Bar. A porphyry occurrence of chalcopyrite–pyrite–magnetite-bearing veinlets/disseminations in the lower parts of the Spach deposit has been described by Hoxha et al. (2005).

Native gold (electrum) occurs as inclusions within chalcopyrite and sphalerite, and tennantite are commonly associated with galena and barite in the uppermost levels of the Munella deposit (Deda et al., 1995). The investigation of massive sulfide ore from the Munella deposit using SIMS methods indicated that significant gold concentrations in pyrite (>1 ppm) are accompanied by significant contents of As; there is a marked covariance with arsenic (Table 5; Figs 7 and 8). The average concentration of invisible gold in coarse-grained pyrite associated with chalcopyrite is 0.22±0.16 ppm. In skeletal pyrite, the concentration varies from 3.99±3.5 ppm in grain cores, decreasing to 0.99±0.33 ppm toward the rims. Copper sulfides carry no gold. Further data are required to define the distribution of gold in a wider variety of sulfide mineralization types.

6. Comparison of the Pindos and Mirdita sulfide ineralization with other submarine sulfide deposits

6.1. Typical sulfide deposits of Cyprus-type

A comparison of the Pindos and Mirdita ophiolite-hosted massive sulfides of Cu–Zn type (the Pb content being negligible) with other massive sulfide deposits of Cyprus-type shows that they differ in several aspects. (1) Host rock-type — the Mirdita sulfide deposits are developed at the contact between andesitic pillow lavas and upper volcanic (ryodacite) rocks, and/or within intermediate to felsic volcanic rocks, whereas typical sulfide deposits of Cyprus-type occur between major basaltic pillow lava sequences, or on top of diabase (massive or pillow lavas), and are directly overlain by pyrite and chalcopyrite content. The lowermost parts are composed of massive pyrite and chalcopyrite. The major ore minerals are pyrite, chalcopyrite and sphalerite, with lesser tennantite–tetrahedrite, and trace galena. At the uppermost, western part of the Munella deposit the pyrite–sphalerite–chalcopyrite association is marked by enrichment in Au, Ag, Se and As. Lesser amounts of tennantite, tetrahedrite and traces of galena are also present. Concentrations of Mo, Sb and Hg are also significant and Bi, In, Ga, Ge, Sn and W have also been detected. The dominant alteration type is silicification, chloritization, zeolitization and epidotization around the massive ores. Commonly, the sericitisation and silicification that surrounds the sphalerite–pyrite veinlets are accompanied by the presence of barite and fluorite. The orebody at the Munella deposit has yet to be exploited, although some development is currently taking place (Table 1; Deda et al., 1995; Hoxha et al., 2005).

Fig. 5. Scatter plot of gold concentration (in arbitrary units) on crystal facets and fracture surfaces of coarse-grained pyrite from Pindos. Crystal facets have much more gold than interior of coarse pyrite crystals. Gold concentration on facets of coarse pyrite is clearly lower compared to the gold content of microcrystalline/fine-grained pyrite.
Fe-oxide sediments. (2) Mineralogical constitution — minerals of the tennantite–tetrahedrite series are characteristic accessory minerals of the Mirdita sulfide ores (Deda et al., 1995), but are absent from the majority of Cyprus-type deposits. (3) Selenium enrichment — the presence of clausthalite (PbSe) in the Pindos sulfides, located within chalcopyrite and sphalerite intergrowths of later stage mineralization cross-cutting ore of an earlier stage (Barlas et al., 2001). (4) Trace element enrichment — gold enrichment is significant in the Kondro (Pindos) and Mirdita (Albania) sulfide ores (up to 3.6 ppm and 60 ppm Au, respectively). Contents of Ag, Zn, Se, As, Mo, Sb and Hg are also significantly higher than in the majority of massive sulfide deposits (Table 1). (5) The presence of submicroscopic gold — which we have documented in As-bearing pyrite of the Pindos and Mirdita ores (Tables 3 and 4). (6) Enrichment in Pt — with up to 1000 ppb Pt being detected in hydrothermally brecciated diabase of the Pindos complex, accompanied by disseminated sulfide mineralization, kaolinite and epidote (Table 1).

6.2. Polymetallic massive sulfide deposits on the modern seafloor

A comparison of ophiolite-hosted massive sulfides with active seafloor hydrothermal systems is included in a number of publications (Constantinou, 1980; Ixer et al., 1986; Robertson and Varnavas, 1993; Hannington et al., 1998; Herzig et al., 2003; Hannington et al., 2005; Franklin et al., 2005). The Mirdita massive sulfides are similar to modern seafloor deposits in terms of: (i) their association with andesitic pillow lavas and intermediate to felsic volcanic rocks (Hannington et al., 1998; Petersen et al., 2002; Hannington et al., 2005); (ii) bulk geochemical composition, including the significant contents of Zn, Ag, Au, As, Sb and Hg, and mineralogy (tennantite–tetrahedrite, selenides and tellurides), although massive sulfides hosted in the Pindos and
Mirdita ophiolites are comparable to seafloor polymetallic sulfides formed in intra-oceanic back-arc spreading centers rather than intra-continental back-arc ridges (Herzig et al., 2003); (iii) elevated Se contents in the Pindos and Mirdita ores (up to 1900 and 980 ppm, respectively) are comparable with those in Cu-rich

<table>
<thead>
<tr>
<th>Pyrite grain ID</th>
<th>Coarse-grained Grain ID</th>
<th>Fine-grained Grain ID</th>
<th>Very fine intergrowths with bornite Grain ID</th>
<th>Bornite grain ID</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>As</td>
<td>Au</td>
<td>As</td>
<td>Au</td>
</tr>
<tr>
<td>21p10</td>
<td>1.79</td>
<td>1850</td>
<td>21p03</td>
<td>3.47</td>
</tr>
<tr>
<td>21p13</td>
<td>0.65</td>
<td>2440</td>
<td>21p04</td>
<td>3.77</td>
</tr>
<tr>
<td>21p20</td>
<td>0.85</td>
<td>110</td>
<td>21p05</td>
<td>6.57</td>
</tr>
<tr>
<td>21p23</td>
<td>0.23</td>
<td>3080</td>
<td>21p06</td>
<td>6.74</td>
</tr>
<tr>
<td>21p24</td>
<td>0.41</td>
<td>620</td>
<td>21p11</td>
<td>2.93</td>
</tr>
<tr>
<td>21p27</td>
<td>0.09</td>
<td>1460</td>
<td>21p12</td>
<td>8.68</td>
</tr>
<tr>
<td>21p29</td>
<td>0.24</td>
<td>1080</td>
<td>21p16</td>
<td>2.71</td>
</tr>
<tr>
<td>21p34</td>
<td>0.41</td>
<td>710</td>
<td>21p17</td>
<td>6.78</td>
</tr>
<tr>
<td>21p35</td>
<td>1.33</td>
<td>250</td>
<td>21p18</td>
<td>2.22</td>
</tr>
<tr>
<td>21p19</td>
<td>2.08</td>
<td>370</td>
<td>21p21</td>
<td>2.45</td>
</tr>
<tr>
<td>21p26</td>
<td>2.78</td>
<td>380</td>
<td>21p28</td>
<td>12.01</td>
</tr>
<tr>
<td>21p32</td>
<td>6.18</td>
<td>1890</td>
<td>21p33</td>
<td>5.38</td>
</tr>
<tr>
<td>21p40</td>
<td>6.8</td>
<td>12900</td>
<td>21p19</td>
<td>2.08</td>
</tr>
<tr>
<td>Average</td>
<td>0.67</td>
<td>1290</td>
<td>4.63</td>
<td>1610</td>
</tr>
<tr>
<td>±λ</td>
<td>0.36</td>
<td>640</td>
<td>1.1</td>
<td>1190</td>
</tr>
</tbody>
</table>

Fig. 6. (a) Photograph of hydrothermal brecciated diabase, underlying the massive sulfide ore of the Kondo area showing disseminated pyrite and vesicles filled by pyrite, quartz, kaolinite and epidote, while chalcopyrite is rare. (b–d) Back-scattered electron images from the diabase breccia, showing (b) remnants of pyrite (py) within magnetite (mt), (c) remnants of pyrrhotite (po) within pyrite surrounding by goethite (goeth) and (d) remnants of pyrite within goethite. Quartz (Qtz) is abundant (b–d).
chimneys at seafloor black smoker sites on the East Pacific Rise (Auclair et al., 1987); and (iv) elevated Pt contents in brecciated pipe-form diabase underlying the massive ore of the Pindos complex, resembling high Pt contents reported in marcasite and chalcopyrite from massive sulfides at 21°N on the East Pacific Rise, although Pt is much higher (up to 1 wt.% Pt) in the latter (Hekinian et al., 1980).

7. Discussion

Most models for volcanic-associated massive sulfide deposits formed predominately on or near the discharge vents of submarine hydrothermal systems favor the circulation of seawater into the oceanic crust at seafloor spreading centers, by analogy with modern submarine hydrothermal activity (Franklin et al., 1981, 2005). Changes in the physical–chemical conditions during mixing of high-temperature (250 to 400 °C) hydrothermal fluids with cold, oxygen-bearing seawater and increasing pH cause sulfide precipitation within the stockwork zone and at the seafloor as massive sulfides (Constantinou, 1980; Franklin et al., 1981; Ixer et al., 1986; Scott et al., 1990; Huston et al., 1995; Hannington et al., 1998, 1999; Herzig et al., 2003). However, the initial composition of ores may be overprinted by post-depositional processes, including hydrothermal reworking and zone-refining, seafloor metamorphism and supergene enrichment (Franklin et al., 1981; Scott et al., 1990; Herzig et al., 1993; Binns and Scott, 1993; Glasby and Notsu, 2003; Hannington, 2003; Layton-Matthews et al., 2005). The characteristic decrease in Cu/Zn ratios in massive sulfide deposits upward and outward from the top of the deposits has been attributed to remobilization of previously deposited sulfides by the action of continued hydrothermal flow or alternatively from an ore solution evolving toward lower Cu/Zn ratios (Franklin et al., 1981; Hannington et al., 1998).

7.1. Genetic significance of the platinum and palladium contents

Platinum and palladium contents in seafloor massive sulfides related to ophiolite complexes are generally very low, but may indicate that PGE are quite soluble under a range of hydrothermal conditions. High Pt (up to 1 wt.%) contents have been reported in marcasite and chalcopyrite from massive sulfides at 21°N on the East Pacific Rise (Hekinian et al., 1980). Also, sulfide deposits at 26°N on the mid-Atlantic Ridge contain significant Pd, ranging from 3 to 1000 ppb (Crocket, 1990). The Pd and Pt content in massive sulfide ores of Cyprus-type from the
Pindos (Kondro) ophiolite complex, Greece, is < 10 ppb for both elements, whereas Au concentrations are up to 3.6 ppm. However, in the hydrothermal breccia underlying the massive ore, Pt reaches values of 1000 ppb; 27 ppb Pd was determined (Table 1). The concentration of Au in massive sulfide ore and Pt in the underlying diabase breccia may reflect differences in the relative solubility of the precious metals, and the extent to which they were saturated in a given hydrothermal solution, as well as the specific deposition mechanisms for each metal (Seward and Barnes, 1997; Wood, 2002). Pan and Wood (1994) pointed out that hydrothermal fluids in equilibrium with pyrite or pyrrhotite and alteration minerals such as chlorite, epidote, albite, calcite, etc., would be incapable of transporting significant amounts of PGE as chloride complexes. These authors instead suggested that a typical seafloor hydrothermal vent fluid could contain a significant amount of Pt and Pd as bi-sulfide complexes and that gold may also be predominantly transported in the form of bi-sulfide complexes. Moreover, they concluded that, under the conditions of their experiments, the solubility of Au as a bi-sulfide complex was three orders of magnitude higher than that of Pt and Pd. Thus, the elevated Pt contents in the mineralized diabase breccia of Pindos compared to massive sulfide ore seems to confirm the higher solubility, and thus further transport, of Au relative to Pt, causing Au enrichment in the massive ore. The presence of pyrrhotite remnants within pyrite, surrounded by hydroxides or magnetite within vesicles filled by pyrite, quartz, kaolinite and epidote may indicate that the Pt-precipitation was favored by weakly acidic and oxidizing conditions (Wood, 2002).

7.2. Mineralogical distribution of gold

The Au grades of VMS deposits may be controlled by temperature, $\alpha S_2$, boiling (related to depth), precipitation mechanisms, and subsequent redistribution (refining zone). High Au content (> 2 ppm) can result from a change of transporting ligand, possibly induced by boiling because of cooling of the fluids during decompression and the large increase in pH and $fO_2$ that accompanies the loss of dissolved gases. As a boiling fluid rises to the seafloor and cools, the base metals carried as chloride complexes at high temperatures may be precipitated within a vertically-extensive stockwork zone. In contrast, gold, which is transported as an aqueous sulfur complex, may be effectively separated from the base metals and concentrated along with other volatile species, such as As, Sb and Hg, above the boiling zone (Huston and Large, 1989; Yang and Scott, 1996; Hannington et al., 1999; Huston, 2000; Moss and Scott, 2001; Pinto et al., 2005; Hannington, 2003; Ihle et al., 2005; Franklin et al., 2005).

Electrum, native gold, Au-tellurides and invisible gold (structurally-bound gold and inclusions of native gold <1000 Å in size) in arsenian pyrite and arsenopyrite have been identified as hosts in Au-bearing volcanic-hosted massive sulfide deposits (Huston et al., 1992; Herzig et al.,
1993; Huston, 2000). According to Huston et al. (1992), in Cu–Au VMS deposits of Eastern Australia, where Au is concentrated along with Cu at the base of the sulfide lens and in the stringer zones, the Au is found as electrum or as Au-tellurides associated with chalcopyrite and/or pyrite, and may have been directly precipitated from chloro-complexes. In Zn–Cu deposits, however, where Au is concentrated with Zn at or near the top of the deposit, Au is hosted in auriferous arsenopyrite and arsenian pyrite in the center of the lens, and as electrum in the barite-bearing top of the lens. In the later case, it has been suggested (Huston et al., 1992) that Au may be co-precipitated into the structure of arsenopyrite and pyrite in the core of the deposit, but toward the top of the deposit. Gold may be precipitated in association with sulfides and/or barite from thio-complexes. In addition, Au was mobilized during deformation of the ore, and was reprecipitated as fine-grained electrum along fractures and boundaries of pyrite grains. In addition, Huston (2000) emphasized that pyrite, in VHMS deposits which had not recrystallized, tends to have higher levels of invisible gold than recrystallized pyrite. More specifically, metamorphic recrystallization can “sweat out” invisible gold from pyrite and arsenopyrite (Larocque et al., 1993), potentially enhancing metallurgical recoveries. Elevated gold contents of bornite-rich massive ore and the association of arsenopyrite hosting invisible gold in the Neves Corvo deposit (Portugal), accompanied by parageneses typical of high sulfidation has been attributed to either a long-lived maturation of the ore-forming system, resulting in extreme zone-refining effects, and/or a late input of an external magmatic fluid component (Relvas et al., 2001; Pinto et al., 2005). Thus, although gold is a common by-product from the mining of VHMS deposits, the mineralogical distribution of gold in submarine ore systems or/and their ancient analogues depends on many factors and its genetic significance still remains unclear.

With respect to the depositional processes controlling the primary occurrence of gold in both the Pindos and
Mirdita massive sulfide ores, apart from rare gold-free that has been identified (Deda et al., 1995; Barlas et al., 1999), the present investigation using SIMS methods revealed the presence of sub-microscopic or invisible gold. This occurs as structurally-bound component within sulfide minerals or as colloidal gold (<0.5 μm) (Chryssoulis, 1989; Tables 3 and 4; Fig. 7). The increasing gold content (up to 15.1 ppm), with decreasing crystal size in fine intergrowths between pyrite and sphalerite, together with the positive correlation between the concentrations of As and Au in pyrite in the above ores, confirms earlier conclusions for distribution of invisible gold in common sulfides, including sediment-hosted, epithermal, and mesothermal gold deposits (Cook and Chryssoulis, 1990; Pals et al., 2003). The greater content of sub-microscopic gold in finer-grained pyrite of the evidently later bornite-rich ore that crosscuts the main earlier stage of the sulfide mineralization, coupled with the relatively high concentrations of Cu, Zn, As, Se, Sb, Sn, In, and high sulfidation mineral assemblages (Tables 1–4) may reflect the direct involvement of magmatic volatiles to the ore-forming hydrothermal system (Sillitoe et al., 1996) and in turn the precious metal endowment in the hydrothermal systems rather than the effects of recrystallization.

7.3. Genetic significance of selenium contents

The distribution of selenium within sulfide minerals can arise from three possible mechanisms: (a) changes in fluid Se/S ratio by sulfide precipitation/dissolution reactions, (b) fractionation of Se with temperature, and (c) fractionation of Se with redox or pH changes (Huston et al., 1995; Layton-Matthews et al., 2005). In the case of the Pindos mineralization, the association of the lowest Au and Se contents in samples dominated by early pyrite versus those characterized by bornite and/or chalcopyrite-(Fe-poor) sphalerite intergrowths of a later stage (Table 1), may suggest either deposition during a later stage, cross-cutting event during the evolution of the mineralized system, or dissolution and re-deposition of Au and Se. With respect to Se-bearing minerals in massive sulfide ores, the absence of discrete selenide minerals in the majority of VHMS deposits, despite their enrichment in selenium, has been attributed to the relatively lower (∼10⁻⁵) values of ΣSe/ΣS ratios in the evolving seawater (Huston et al., 1995; Xiong, 2003). The minimum ΣSe/ΣS ratios in mineralizing fluids for the occurrence of discrete selenides favor values of at least ∼10⁻⁴ to ∼10⁻³, at relatively higher (>300 °C) temperatures (Xiong, 2003). Thus, the occurrence of the selenide, clausthalite, and traces of galena in fine-grained intergrowths of chalcopyrite and Fe-poor sphalerite may also reflect a magmatic fluid contribution.

7.4. Characteristics of a transition to epithermal type?

Apart from the mineralogical and compositional variations implying changing chemistry of the hydrothermal fluids during sulfide deposition or/and redeposition, we note: (a) an increasing trend of the average Zn, Au, Ag, As, Se, Sb, Mo and Hg contents from the Othrys to Pindos and Munella (Mirdita) massive sulfide ores; (b) elevated concentrations of these elements in the massive sulfide ores of both Cyprus and Fe–Cu–Ni–Co type hosted in the Pindos complex compared to those in the Othrys complex (Tables 1 and 2; Economou and Naldrett, 1984; Rassios, 1990). These differences may be related to the lithology, geochemistry and probably the geotectonic setting of those ophiolite complexes. Volcanogenic massive Cu–Zn–(Pb) ores are primarily hosted by bimodal, mafic–felsic volcanic successions, and are typically associated with felsic volcanic rocks (Franklin et al., 2005). The microplate tectonic setting that characterizes the present-day western Pacific (Hannington et al., 2005) has also been suggested for the formation of the Tethyan ophiolites (Jones and Robertson, 1991; Shallo, 1994). In such a complex environment, rapid changes from collisional to extension and rifting, and back to a highly compressed system are common; diverse seafloor hydrothermal systems may occupy different volcanic rocks in close proximity to one another (Hannington et al., 1999; Hart et al., 2004; Hannington et al., 2005). As the result of arc, fore-arc and back-arc rifting, subsidence and thinning of crust caused bimodal mantle-derived mafic and crystal-derived felsic magmatism (Hart et al., 2004; Hannington et al., 2005).

A relationship between seafloor hydrothermal activity and submarine porphyry-Cu mineralization is uncertain (Sillitoe, 1980; Hannington et al., 2005). VMS, porphyry-Cu and epithermal deposits occur only occasionally in a close proximity, due probably to their juxtaposition (Franklin et al., 2005). Furthermore, it has been suggested that Au enrichment in some VMS deposits may be related to overprinting by a contemporaneous epithermal event (Scotney et al., 1999). Porphyry-type mineralization seems to be present within gabbro–plagiogranites of the lower succession of the Spach deposit (Mirdita). Stockwork-type mineralization consisting of chalcopyrite, pyrite and magnetite assemblages in porphyry dikes, characterized by intense silification and quartz–chlorite–epidote, actinolite assemblages, is widespread (Kyritsis, 1993;
The presence of porphyry-Cu intrusions within lower sequences of the Mirdita complex is obviously related to a later, distinct tectonic–magmatic event. Nevertheless, the spatial association of probable porphyry-Cu mineralization with the Mirdita ophiolite may reflect a shallow type submarine mineralization (Hannington et al., 1999; Franklin et al., 2005).

Taken together, the presence of (a) hydrothermal breccia underlying massive ore at Pindos, which is accompanied by acidic alteration type, (b) the Au-rich association of pyrite, sphalerite and chalcopyrite with high sulfidation Cu-minerals (tennantite–tetrabedrite), (c) co-precipitation of submicroscopic gold with arsenian pyrite, (d) elevated contents of As, Au, Se, Sb, Hg, Mo, Bi, In and Sn in the uppermost parts of the Mirdita (Munella) deposits and (e) the association of the latter with intermediate to felsic-dominated volcanic successions, resembles a VMS-epithermal transition model (Hannington et al., 1999, 2005). Based on geological, mineralogical and geochemical data on polymetallic sulfides at the modern seafloor, it has been widely accepted that deposits with the highest average Au grades are associated with intermediate to felsic-dominated volcanic successions. In this regard, subduction-related spreading centers are the closest analogues of the majority of the most important land-based deposits, instead of mid-ocean ridge basalts (Herzig and Hannington, 1995). The relatively high trace element contents (Au, Ag, As, Se, Hg, Sb and Mo) that accompany Cu–Zn sulfide ores in the Mirdita deposits, coupled with volcanic successions of intermediate to felsic composition, may provide a link to a felsic magmatic source similar to modern spreading centers and constitute a wide range of potential exploration target (Yang and Scott, 1996; Hannington et al., 2005).

8. Conclusions

Available geological, petrological, mineralogical and geochemical characteristics of the Pindos and Mirdita ophiolites and related sulfide ores lead to the following conclusions:

(1) Gold in both Pindos and Mirdita ores occurs as submicroscopic or invisible gold, including solid solution gold, colloidal gold and surface-bound gold in arsenian pyrite, chalcopyrite and bornite grains, and rarely as fine-grained electrum, suggesting that Au is essentially found as structurally-bound gold in pyrite.

(2) The gold content in coarse-grained pyrite is up to 1.02 ppm in the Pindos massive ore and 0.22 ppm in the Mirdita ore, while there is an increasing gold content (up to 15.1 ppm) with decreasing crystal size in fine intergrowths between pyrite and sphalerite, cross-cutting ore of an earlier stage of the Pindos massive ore.

(3) The increasing trend of average Zn, Au, Ag, As, Se, Sb, Mo and Hg contents from those hosted in the Othrys complex and other Cyprus-type deposits, and resembles those of polymetallic sulfides at the modern seafloor.

(4) The significant Pt-enrichment (up to 1000 ppb Pt) in the diabase hydrothermal breccia, underlying the massive mineralization, the presence of claushtalite in association with galena at Pindos, the dominance of Au as structurally bound in pyrite, and the presence of high sulfidation Cu-minerals, may provide evidence for substantial contributions from magmatic fluids.

(5) The Mirdita sulfide deposits hosted in intermediate to felsic-dominated volcanic successions of a considerable thickness are associated with ophiolites formed during the initial stages of subduction (fore-arc setting), and are the closest analogues to polymetallic sulfides associated with felsic volcanic rocks at the modern seafloor.

Acknowledgements

The University of Athens is greatly acknowledged for the financial support of this work. Many thanks are expressed to Drs. J.P. Vaughan, Curtin University of Technology, Australia, and Stephen Roberts, University of Southampton, for their constructive criticism and linguistic improvement of an earlier draft of the manuscript. Mr. E. Michaelidis, University of Athens, is thanked for his assistance with the electron probe analysis.

References


Large, R.R., Huston, D.L., McGoldrick, P.J., Ruxton, P.A., McArthur,

Moss, R., Scott, S.D., 2001. Geochemistry and mineralogy of gold rich

Pals, D.W., Spry, P.G., Chryssoulis, S., 2003. Invisible gold and

100

M. Economou-Eliopoulos et al. / Ore Geology Reviews 33 (2008) 81–100


aqueous bisulfide solutions. II Results at 200 °C to 350 °C and saturated vapour pressure. Mineralium Deposita 29, 373–390.


